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Pollution assessment models of surface soils in Port Harcourt city, Rivers State, Nigeria

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ABSTRACT

Environmental pollution has resulted in several health and physiological problems in both, plants and animals. This has witnessed growing number of models for assessment purposes. Some of these provide useful information, and reduce large data for easier understanding by policy-makers. In the current study of pollution, we used data from four locations: Oil Market, Trans Amadi, Borrokiri and GRA in Port Harcourt, and a control taken from Federal Land Resource Umuahia (FLRU). A total of 25 composite soil samples were analyzed for physicochemical parameters and heavy metals, by means of a 969 Unicam AAS model series. The data obtained were then subjected to index models. Results showed iron (Fe) to be most abundant metal, ranging from 10.44 to 19.54 mg/kg, then Ni (8.03 to 13.6 mg/kg), Cd (3.96 to 5.41 mg/kg), Pb (1.36 to 7.64 mg/kg), Zn (0.09 to 7.24 mg/kg), Cu (0.16 to 0.32), and As (0.07 to 0.11 mg/kg). All metal concentrations were below permissible limits set by NESRA. Contamination factor (C_f) and Igeo revealed moderate to heavy contamination by Cd and Zn. Anthropogenicity revealed that increasing metals in the environment are largely from anthropogenic inputs. The Pollution Index revealed that soils were unpolluted (PLI < 1) with the heavy metals. Furthermore, the Sodium absorption ratio showed that the soils are less sodic and could be good soils for plant growth. All four sites showed a linear relationship between anthropogenicity and geo-accumulation indexes, and so both indexes furnish basically the same information However, pollution from these metals in the study area should be under routine check for possible pollution in the near future, as some metals showed elevated concentrations above background values.

***Keyword*:** Anthropogenic, Contamination, Pollution indices, Residential area

1. INTRODUCTION

Man is dependent on the environment for his daily activities. Therefore, the quality of the top soil of any environment is very important to man. Over 45% of the world's total population currently resides in urban areas, and this figure is projected to surpass the majority benchmark, reaching 60% by 2030 (United Nations, 2001). This increase in population plays an important role in polluting the environment and causes severe degradation in pedosphere, hydrosphere, and atmosphere. Pollution in the environment is the unfavourable alteration of our environment as a result of wastes from man's activities, changes in radiation levels, physico-chemical characteristics and abundance of organisms in a harmful way (Miller, 1988; Adewoyin *et al*., 2013). However, a pollutant is a substance that occurs in the environment, at least in part, as a result of human activities, and which has deleterious effect on the environment (Bayero, 2004; Adewoyin *et al*., 2013).

Soil is the loose material that covers the land surfaces of earth and supports growth of plants (Enyoh *et al*., 2017) and human activities. Over the past few decades, environmental quality of urban soil has been closely related to human health and so people have become more concerned about the potential pollution of soil around them (Annao *et al*., 2008; Zakir *et al*., 2008, and Verla *et al*., 2015). Soil pollution arising from socioeconomic activities of man may threaten human health if not properly checked (Verla *et al*., 2015). It is also a natural reservoir of metals whose concentrations are associated with several factors such as biological and biogeochemical cycling, parent material and mineralogy, soil age, organic matter, soil pH, redox concentrations, and microbial activities (Obasi *et al*., 2012). Knowledge of soil characteristics and heavy metal levels is important for safety policy formulation and awareness in urban soils.

However, as a result of the increasing rate of industrialization in Nigeria, a lot of harmful substances are now being discharged into the environment. Port Harcourt is an example of an industrialized location in Nigeria**,** where population and traffic densities tend to be high, and also housed two oil refineries, two major airports, sea ports and major industrial estates, amongst others**.** These have resulted to increased anthropogenic activities such as agricultural practices, industrial activities, energy consumption and waste disposal methods which lead to large release of heavy metals into soil, thus leading to the contamination of the soils (Ndiokwere and Ezehe, 1990; Eja *et al*., 2003; Ololade *et al*., 2007; Ebong *et al*., 2007, 2008, and Obasi *et al*., 2012). The poor management of waste or effluents could create a number of adverse environmental impacts, including wind-blow litter, attraction of mice and pollutants such as leachate, which can pollute underground soil bed, and / or aquifer (Abdulssalam, 2009; Osazee *et al*., 2013). Therefore, the need to understand urban environmental quality and its associated implications for the environment and human health is important.

Several studies reported on Port Harcourt soil have been mostly on the effects of dumpsites (Ogbonna *et al*., 2002; Ogbonna *et al*., 2009, and Ukpaka and Pele, 2012). However, no study, as far as it could be established, have been reported on the general pollution status of soils from the city. Godson (2004) studied the quality of soil near a chemical fertilizer industry at Port Harcourt, Nigeria and showed that the soil environment around was the most affected with the highest mean phosphate and potash levels of 494.5mg/kg and 32.3mg/kg, respectively. The presence of metals and other mineral elements at various concentrations revealed that the industrial wastes contaminated the soils. The author also remarked that the impact of the pollutants, as assessed, appears to be more on the soil. Ukpaka and Pele (2012) performed elemental analysis of soil characteristics due to municipal solid waste in Port Harcourt City and found to contain significant amount of toxic and essential elements**.** Edori and Kpee (2017) did an index models assessment of heavy metals in soils within selected abattoir and reported that the soil showed high abundance of iron (Fe) and slight contamination by copper (Cu). However, the general view of pollution index (PI), geo-accumulation, and enrichment factor showed that the soil was free from pollution (Edori and Kpee, 2017). The present distribution of metals in the soil can serve as an indication of time, history, and extent of pollutants discharged in the area. Assessing the problems caused by contaminated soils typically involves soil chemistry as well as laboratory and field studies to fully assess the extent and significance of any adverse environment effects (Osakwe *et al*., 2003**;** Akpoveta *et al*., 2010) of industrialization. Therefore, the aim of this study was to examine the physicochemical properties and heavy metal levels in soils of Port Harcourt city with a view to establish the pollution or contamination status of the soils as a result of anthropogenic input. This study will be build on the past works conducted in various parts/areas of Port Harcourt city by presenting concrete and reliable data from the analysis of soil samples in selected sites that will serve as a benchmark for the future studies on soils in Port Harcourt city

2. MATERIAL AND METHODS

2. 1. Study area

The study area is Port Harcourt metropolitan city in Nigeria (**Figure 1**). Called the oil city, it is well known with sea port and lots of goods imported through the Port Harcourt Warf. Many industries exist in Port Harcourt, ranging from small sized industries to multinational companies such as Shell Petroleum Development Corporation (SPDC), with its numerous activities involving oil exploration and refining of oil products, cement, glass, and agro industrial companies. Four sampling sites include Trans Amadi (TA) and Oil Mill market (OM) for the industrial road area and GRA Diobu (GRA) and Borokiri (BO) for the residential areas. The control was taken from Federal Land Resource, Umuahia (FLRU). Three composite samples were collected from five different sites. At each site, a W-shaped line was drawn on a 2×2 m surface and the top (0–10 cm depths) soil samples were collected using a hand-held Auger (Verla *et al*., 2015; Enyoh *et al*., 2017). The soils were pooled, treated to coning and quartering to obtain a composite sample of each site. The soil samples were air dried, sieved with a 2 mm mesh size, and stored in black polythene bags in triplicate, until analysis commenced (Udo and Fagbami, 1979; Taofeek and Tolulope, 2012).

2. 2. Soil analysis

pH measurements were carried out in deionized water (50 mL), after stirring (with a hand-held polypropylene rod for 15 min) the air dried sample portion of 2.0 g for an hour. Using the same solution, the electrical conductivity was measured by means of Yokogawa conductance Sc. 82 conductivity meter. The organic matter content was determined as a weight loss by weighing the sample before and after heating at 500 °C for 2 hours (Ano, 1994; Sezgin *et al*., 2003; Enyoh *et al*., 2017). Particle size distribution was determined by the sedimentation method (Mustapha, 2003; Abechi *et al*., 2010). 2 g of each sample were mixed with 20 mL of 4 M HNO_3 at 90 °C for 4 hours. The mixtures were filtered into 25 mL standard flask and solution made up to mark with ionized water. Appropriate standard solutions were made and concentrations of Pb, Cd, Cr, Fe, Zn, Ni, and Cu, and As in the digest were determined using 969 Unicam ASS.

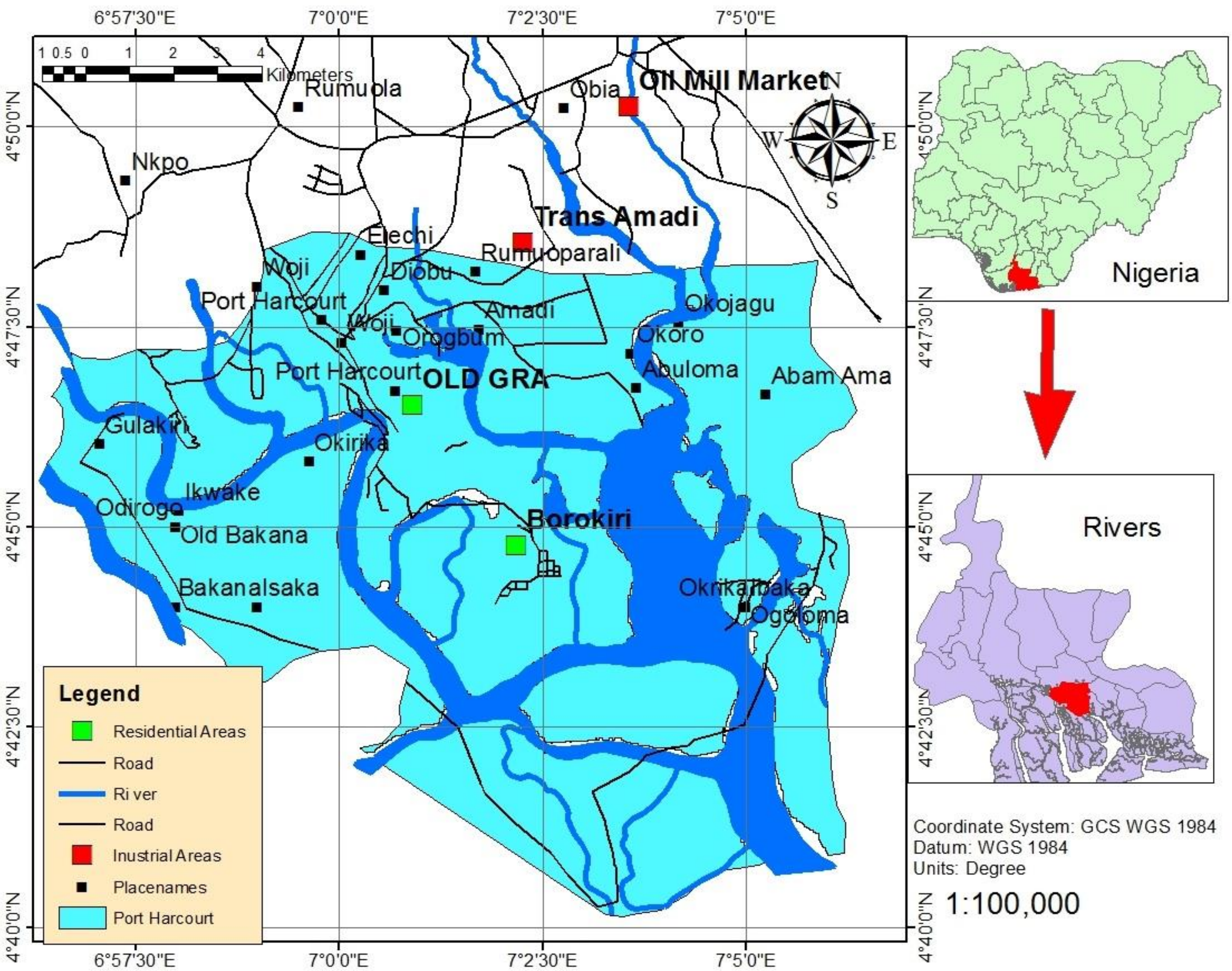


Figure 1. Map of Port Harcourt area showing sampling location

2. 3. Data analysis

The data was analysed using LSD at 5% level of probability according to the Michigan State University software program for the design and analysis of agronomic research experiment (MSTACC) statistical package. A two-tailed Pearson correlation coefficient was determined for heavy metals.

2. 4. Pollution index models

In order to assess the heavy metal pollution levels and the extent of contamination in the soil samples, the data obtained for the heavy metal concentrations were used to calculate the

Contamination Factor (*CF*), the Pollution Load Index (*PLI*), Geo-accumulation Index (Igeo), and the Anthropogenicity (Apn).

Assessment of the extent of soil contamination or enrichment with heavy metals was carried out using the contamination factor (*CF*) estimation, as proposed by Forstner and Calmano (1993). *CF* is obtained by dividing the concentration of the elements by their background concentration, as presented in following:

$$CF = \frac{C_m}{C_b} \tag{1}$$

where C_m is the concentration of the metal in the soil and C_b is the concentration of the metal in the background. The background concentrations were taken as the target value (mg/kg) of the Department of Petroleum Resources. These values are: Fe – 38,000, Zn - 140, Pb - 85, Co - 20, Cu - 36, Cr - 100, Ni - 35, Mn - 850, As - 1.0 and Cd - 0.8 (DPR, 2002).

The Pollution Load Index (PLI)**,** as proposed by Thomilson *et al*. (1980), was used to assess the quality of soil in a polluted site. PLI is obtained as a product of the measured contamination factors of the different metals in the soil samples. Generally, the *PLI* is estimated using the following:

$$PLI = (CF_1 X\ CF_2 X\ CF_3 \ldots\ldots CF_n)^{1/n} \tag{2}$$

where *n* is the number of metals considered in the study, and *CFi* is the contamination factor for each individual metal. The *PLI* provides a comparative means for assessing a site quality.

The Geo-accumulation Index (Igeo) was introduced by Müller (1981) to assess the extent of metal pollution in soil samples. The Igeo was estimated using the following Eq. (3):

$$\mathrm{Igeo} = \log 2 \left(\frac{C_\mathrm{m}}{1.5 C_\mathrm{b}}\right) \tag{3}$$

where C_m is the concentration of the metal in the sample, C_b is the background value of the metal, 1.5 is the background matrix correction factor due to lithogenic effects; hence, this index is used to analyze natural fluctuations in the content of a given substance in the environment and very small anthropogenic influences. The background value taken is considered from world average value in shale (mg/kg) of the metals determined in the study.

The values are Fe = 47,200, Zn = 95, Pb = 20, Co = 19, Cu = 45, Cr = 90, Ni = 68, Mn = 850, As = 13 and Cd = 0.3 (Edori and Kpee, 2017).

Anthropogenicity (Apn) measures directly the anthropogenic influence on the metal concentrations in the soil:

$$\mathrm{Apn} = \frac{\mu}{Cb} \times 100 \tag{4}$$

The μ is current or measured concentrations of metals in the soil, while C_b is the background value, considered from world average value in shale (mg/kg) stated above.

Sodium absorption ratio (*SAR*) was calculated according to Verla *et al*., 2015, Mmolawa *et al*., 2011.

$$SAR = \frac{Na}{\frac{\sqrt{(Ca+Mg)}}{2}} \quad (5)$$

3. RESULTS AND DISCUSSION

3. 1. Physico-chemical properties

The results for the physico-chemical properties in soil samples, taken from Port Harcourt areas during January 2014, are presented in **Table 1** below.

Table 1. Physicochemical properties of soil samples.

Parameter	Location					Arithmetic mean	Geometric mean	FLRU
	OM Market	Trans Amadi	Borokiri	GRA	SDV			
pH	6.00	6.30	5.63	6.47	0.37	6.10	6.09	6.13
H^+	2.73	0.79	1.43	3.06	1.07	2.00	1.75	0.84
EC (S/cm)	0.51	0.82	0.09	0. 31	0.50	0.47	0.34	0.32
AP	10.5	16.31	14.65	13.57	0.37	13.76	13.58	20.10
NO_3^- (mg/kg)	0.42	0.33	0.61	0.57	0.33	0.48	0.47	0.28
SO_4^{2-} (mg/kg)	1.96	5.84	4.36	5.81	0.31	4.49	4.13	3.22
TN	0.23	0. 35	0.22	0.18	0.29	0.21	0.21	0.19
B.Sat (%)	34.30	27.41	43.01	50.31	0.28	38.76	37.77	17.81
OC (%)	3.98	3.52	1.73	2.05	0.26	2.82	2.65	1.01
Sand (%)	22. 87	6.057	91.53	85.03	0.25	60.87	36.12	13.00
Silt (%)	68.27	26.60	6.70	10.63	0.25	28.05	18.96	57.27
Clay (%)	8.90	6.70	1.73	4.30	0.24	5.41	4.59	29.73
THC (%)	7.57	6.77	4.70	7.27	0.23	6.58	6.47	6.73

EC = Electrical conductivity, AP = Available Phosphorus, TN = Total Nitrogen, B.Sat = Base Saturation, OC = Organic Carbon, THC = Total Hydrocarbon

The soil pH obtained in this study generally hovers around the slightly acidic to neutral range, which ranges from 5.63 at Borrokiri to 6.47 at GRA with arithmetic and geometric mean of 6.10 and 6.09, respectively**.** These values are expected as most soils in the tropics have their ranging from acidic to slightly neutral (Alloway, 1997 and Okoro *et al*., 2015)**.** In comparison, with the control soil (FLRU), the soil has lower pH. Although all soils showed acidity, this is in conformity with soil pH reported in other studies, conducted in other areas in Nigeria (Verla et al., 2015; Ahukaemere *et al*., 2016; Enyoh et al., 2017). Ahukaemere *et al.* (2016) reported that the soil acidity could be due to the parent material from which the soils are derived. However, only Trans Amadi and GRA showed higher acidity to the control soil. Ranking in decreasing order of soil acidity is as follows: GRA > Trans Amadi > FLRU (control) > OM Market > Borrokiri. The soil pH is a function of H^+ and plays an important role in metals availability for uptake by plants and animals.

The electrical conductivity (*EC*) is a measurement of the dissolved material in an aqueous solution, which relates to the ability of the material to conduct electrical current through it (Enyoh *et al*., 2017).The (*EC*) measurements show that samples from Trans Amadi recorded the highest (0.82 S/cm) and GRA (0.31 S/cm) recorded the lowest values. However, in comparison with the control soil (0.32 S/cm), arithmetic (0.47 S/cm) and geometric values (0.34 S/cm) were higher. The observed *EC* in this study could have been due to the textural class of the soil. *EC* usually correlates strongly to soil texture and cation exchange capacity (CEC) (Verla *et al*., 2015). This is in conformity with the concentrations of cations obtained in this study (**Table 2**).

Table 2. Mean total metal concentrations (mg/kg dry matter)

Metal Symbol	Location					Arithmetic mean	Geometric mean	FLRU	NESRA Standard
	Oil Mill Market	Trans Amadi	Borokiri	GRA	SDV				
K	9.11	7.81	8.36	4.37	2.10	7.41	7.14	4.02	-
Na	13.01	10.33	10.26	11.25	1.28	11.21	11.16	10.27	-
Ca	28.05	20.11	26.31	27.80	3.72	25.57	25.34	52.30	-
Mg	9.30	8.31	9.36	13.61	2.36	10.15	9.96	11.6	-
Al	0.30	2.30	1.40	1.21	0.82	1.3	1.04	0.84	-
Cd	5.41	4.43	3.96	4.06	0.66	4.47	4.43	1.32	3
Cr	0.73	0.21	0.11	0.46	0.27	0.38	0.30	0.24	100
Fe	10.44	19.54	13.06	18.15	4.27	15.3	14.83	9.87	20

Cu	0.32	0.11	0.21	0.16	0.09	0.20	0.19	0.11	100
Ni	9.46	13.6	9.11	8.03	2.44	10.05	9.85	8.74	68
Zn	0.09	7.24	0.46	4.71	3.45	3.13	1.09	3.11	421
As	0.11	0.11	0.11	0.07	0.02	0.10	0.10	0.03	20
Pb	7.64	5.34	1.36	6.48	2.73	5.21	4.35	1.10	-

Organic carbon (OC), total nitrogen (TN) and available phosphorus (AP) were 2.82%, 0.21%, and 13.76%, respectively. Organic carbon (OC) content of the soil was rated moderate (> 2%), while TN value was rated medium (Osakwe, 2014), AP was rated high. The OC, TN and AP obtained in Port Harcourt soils were higher (OC and TN) and lower, respectively, when compared with the control soil (1.01%, 0.19% and 20.10%) from Umuahia, Abia state. The presence of Nitrogen and Phosphorus are indicators of agrochemical usage on the soil. This is similar to the earlier study conducted near a chemical fertilizer industry at Port Harcourt, Nigeria by Godson (2004).

Nitrate and sulfate level obtained in the study ranges from 0.33 at Trans Amadi, to 0.61 mg/kg at Borokirri, and 1.96 at OM Market to 5.84 mg/kg at Trans Amadi, respectively. In comparison with the control soil, the arithmetic mean is higher 0.48 mg/kg > 0.28 mg/kg for nitrate and 4.49 mg/kg > 3.22 mg/kg for sulfate in the soils, respectively. Burning of fossil fuels in power plants and cars, and all internal combustion engines that usually result in the production of nitric acid ammonia as air pollution are sources of nitrate in the environment. Industrial applications of nitrate as an oxidizing agent, in the production of explosives and as purified potassium nitrate for glass making are also potential sources of environmental nitrate (Morgan *et al*., 1989). When nitrogen undergoes natural processes of photochemical oxidation during lightening and thunderstorm, it gives oxides of nitrogen, which are the source of nitrate in the environment (Udofia, 2005). When in excess in the environment, it can be hazardous to health, especially for children and pregnant women.

The sulfate concentration in the soil solution is a good indicator of sulfur availability to plants. Sulfur is an essential micronutrient required by plants and animals. Under normal agricultural conditions, the quantity of sulfur released from organic matter and oxidized to the plant–available sulfate form depends to a great extent on the amount and sulfur status of the organic matter present, and on satisfactory microbial environment including soil pH, temperature, and water status (Isirimah *et al*., 2003). Deficiency of sulfur in the soil causes initial yellowing of young leaves, spreading to whole plant while excess of sulfur in the soil may cause premature dropping of leaves in plants (Osakwe, 2014).

The base saturation obtained in this study ranges from 27.41% at Trans Amadi to 50.31% at GRA and is consistent with the mean pH value recorded in the study, since percentage base saturation means the amount of the cation exchange capacity, not holding potential acidity. This is similar to the values obtained by Osakwe (2014). The percentage base saturation expresses the relative contribution of the exchangeable bases to the overall exchange capacity and it is an important property of soil acidity, useful for soil fertility evaluation, because a high percentage base saturation implies desirable nutrient levels and low soil acidity. The base saturation was generally higher than control soil (17.81%).

The textural class of the soil obtained using the USDA soil textural triangle showed that the soils were sandy in nature (Table 1) from the arithmetic and geometric means. This phenomenon is in agreement with reports by Oyedele *et al.*, (2008), Ideriah *et al.*, (2010), Eneje and Lemoha (2013), and Osazee *et al*., (2013), However, OM Market and Borrokiri were silty in nature, which are in support of earlier report by Ogbonna *et al.*, (2009), who indicated that majority of top soil samples collected from waste dump sites in Port Harcourt, Rivers State, Nigeria, were silty in nature. Silt is a granular material of a size between sand and clay, whose mineral origin is quartz and feldspar, and may occur as a soil (often mixed with sand or clay).

3. 2. Total heavy metal contents

Arithmetic and geometric mean concentration of cations and heavy metals in Portharcourt soils was calculated from the mean values of each element determined for every studied site. The calculated arithmetic mean concentrations of K, Na, Ca, Mg, Al, Cd, Cr, Fe, Cu, Ni, Zn, As, and Pb were 7.41, 11.21, 25.57, 10.15, 1.3, 4.47, 0.38, 15.30, 0.20, 10.05, 3.13, 0.10, and 5.21mg/kg, respectively. For comparison, in the control soil (*i.e*. Federal Land Resource, Umuahia, FLRU) analyzed, the arithmetic mean concentrations of K, Na, Ca, Mg, Al, Cd, Cr, Fe, Cu, Ni, Zn, As, and Pb were 4.02, 10.27, 52.30, 11.60, 0.84, 1.32, 0.24, 9.87, 0.11, 8.74, 3.11, 0.03, and 1.10 mg/kg, respectively, which are similar with those in the obtained from Portharcourt soils studied.

Furthermore, it is observed that the concentrations of heavy metals in the studied soils are within permissible limits for heavy metals in soil, as compared to National Environmental Standard and Regulation Agency, NESRA, (2011).

According to Ure and Berrow (1982) the geometric mean concentration of Zn, Cu, Cd and Pb in world soils was 50, 25, 0.62 and 29 mg/kg, respectively. In comparison with the mean geometric concentration of Zn, Cu, Cd and Pb obtained here (1.09, 0.19, 4.43 and 4.45 mg/kg, respectively), these indicate that the examined soils have not been contaminated. Comparison with literature data also revealed that our data for urban area are much lower than those presented in Czech Republic (Strnad *et al*., 1994) and Italy (Imperato *et al*., 2003) indicating that soils of PortHarcourt are not polluted by heavy metals.

However, a critical look at Table 2 showed elevated mean concentrations of cations and heavy metals of Na, Ca, Mg, Fe, and Ni at various locations in the study. Therefore, they are below permissible values and always in the range of the determined contents of heavy metals for agricultural soil in Spain (Zurero-Cosano *et al*., 1989), and USA (Holmgren *et al*., 2003).

The low contents of metals in the soil could be attributed to the Organic Carbon (OC%) contents in the soil obtained in this study (Table 1), as soil OC contents is known to form complexes with metals (Enyoh *et al*., 2017) and impedes bio-availablity of metals (Verla *et al*., 2015). In addition, soil pH (5.30 to 6.47, Table 1) could have an effect on the solubility of metals retention in soil: the greater retention and lower solubility of metal occurs at high soil pH (Škrbić and Miljević, 2002)

Table 3. Spearman's correlation coefficient between metal concentrations at 5% significance level.

Metal	K	Na	Ca	Mg	Al	Cd	Cr	Fe	Cu	Ni	Zn	As	Pb
K	1												
Na	0.801	1											
Ca	0.722	0.967	1										
Mg	0.407	0.850	0.910	1									
Al	0.126	0.077	0.012	0.136	1								
Cd	0.862	0.986	0.917	0.757	0.089	1							
Cr	0.165	0.422	0.362	0.297	-0.705	0.437	1						
Fe	0.400	0.685	0.639	0.770	0.703	0.651	-0.106	1					
Cu	0.696	0.687	0.694	0.405	-0.596	0.699	0.675	-0.057	1				
Ni	0.793	0.778	0.649	0.543	0.602	0.826	-0.016	0.824	0.238	1			
Zn	-0.342	-0.165	-0.277	0.012	0.744	-0.153	-0.321	0.539	-0.774	0.285	1		
As	0.971	0.871	0.800	0.560	0.293	0.910	0.092	0.604	0.590	0.891	-0.176	1	
Pb	0.230	0.578	0.452	0.487	-0.238	0.600	0.853	0.354	0.425	0.362	0.153	0.258	1

The spearman's correlation coefficient model was used to show relationship or association between metals in Port Harcourt soil, and the coefficients are shown in **Table 3** above. The inter-relationship or association between the metals showed close association between Cd and Na (0.99), Cd and Ca (0.92), As and K (0.97) and Cd and As (0.91) which showed strong correlation significance. Most metal pairs were positively correlated which is an indication that most metals have common contamination source. However, Zn showed negative correlation with K, Na, Ca, Cd, Cr, and Cu. Positive correlation indicates similar source of contamination while negative indicates dissimilar source of contamination.

3. 3. Pollution assessment models

Contamination factor (*CF*) and Geo-accumulation Index (Igeo) are indicators used to assess the presence and intensity of anthropogenic contaminant deposition on surface soil (**Table 4**). These indexes of potential contamination are calculated by the normalization of one metal concentration in the topsoil respect to the concentration of a reference element (Barbieri, 2016).

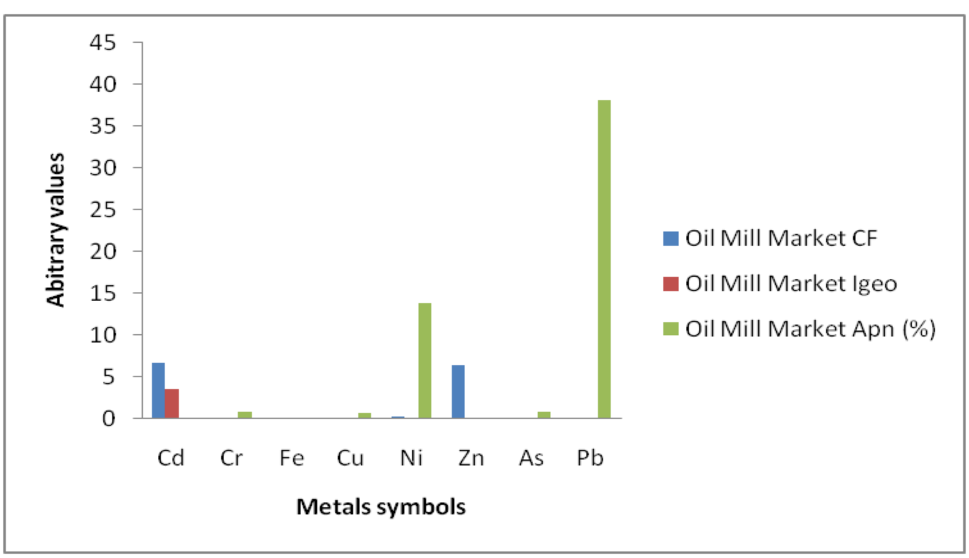
Table 4. Showing assessment models result for Port Harcourt soils.

Metals	Oil Mill Market			Trans Amadi			Borrokiri			GRA		
	CF	**Igeo**	**Apn (%)**	***CF***	**Igeo**	**Apn (%)**	***CF***	**Igeo**	**Apn (%)**	***CF***	**Igeo**	**Apn (%)**
Cd	6.76	3.62	1803	5.54	2.96	1476	4.95	2.65	1320	5.075	2.72	1353
Cr	0.0073	0.00163	0.81	0.0021	0.000046	0.23	0.0011	0.000241	0.12	0.0046	0.00102	0.51
Fe	0.00027	0.00004	0.02	0.0005	0.000080	0.04	0.00034	0.000060	0.03	0.00048	0.000080	0.04
Cu	0.0089	0.00142	0.71	0.0031	0.000482	0.24	0.0058	0.000944	0.47	0.0044	0.000723	0.36
Ni	0.27	0.028	13.91	0.39	0.000402	0.20	0.26	0.027	13.40	0.23	0.024	11.81
Zn	6.42	0.00018	0.09	0.052	0.02	7.62	0.0033	0.000964	0.48	0.034	0.0099	4.96

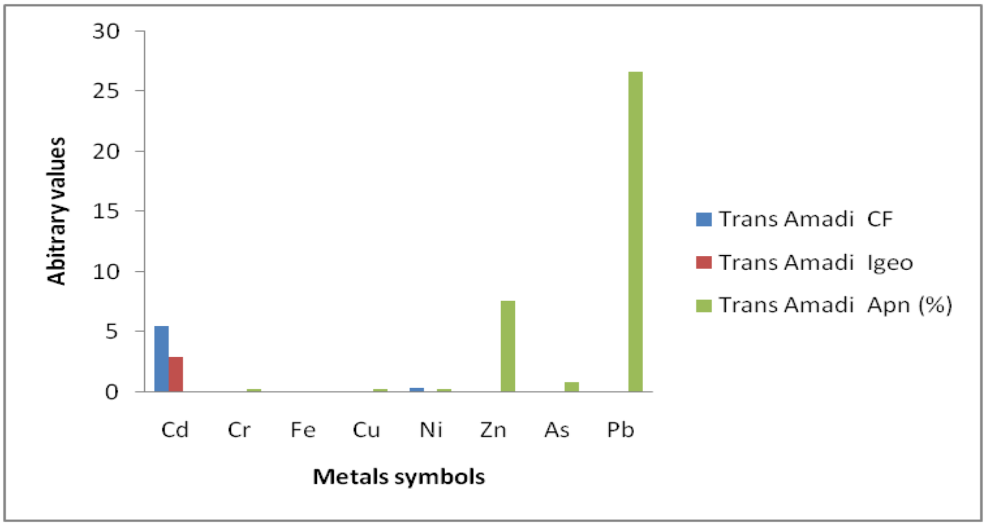
As	0.11	0.00171	0.85	0.11	0.00171	0.85	0.11	0.00171	0.85	0.07	0.0011	0.54
Pb	0.089	0.077	38.20	0.062	0.054	26.70	0.016	0.014	6.80	0.08	0.065	32.40
PLI	0.082			0.036			0.019			0.035		
SAR (Cmol/kg)^{05}	4.25			3.02			3.41			3.49		

*CF = Contamination factor, Igeo = Geo accumulation Index, Apn = Anprogenicity, *PLI* = Pollution index, SAR = Sodium Absorption Ration.

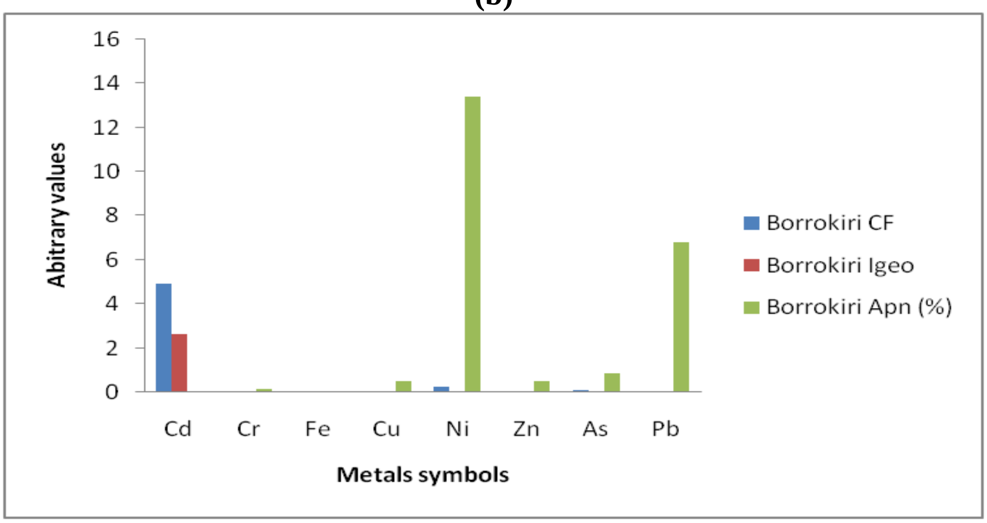
The contamination factors (**Figure 2**) were categorized according to Mathias and Stephen (2016). Values < 1 are low contamination, 1≤CF<3 are moderately contaminated, 3≤ CF ≤ 6 are considerably contaminated, and ≥ 6 very highly contaminated. Therefore, from the study, Oil Market is highly contaminated with Cd (6.76) and Zn (6.42), Trans Amadi, Borrokiri and GRA were all considerably contaminated with cadmium, showing high values of 5.54, 4.95, and 5.08, respectively. Cadmium (Cd) is one of the most toxic elements to which man can be exposed at work or in the environment. Once absorbed, Cd is efficiently retained in the human body, in which it accumulates throughout life. It is primarily toxic to the kidney, especially to the proximal tubular cells, the main site of accumulation. Cd can also cause bone demineralization, either through direct bone damage or indirectly as a result of renal dysfunction (Bernard, 2008).



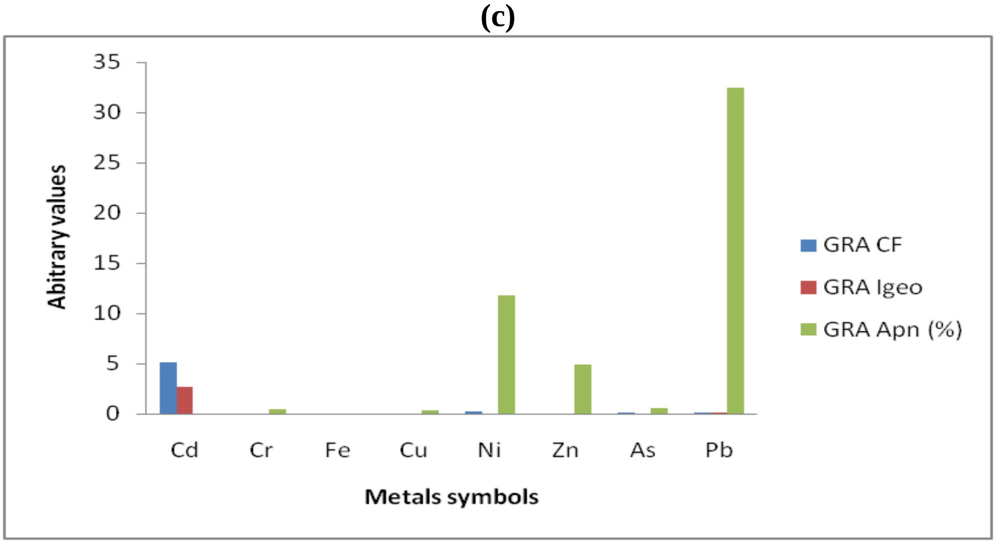
(a)



(b)



(c)



(d)

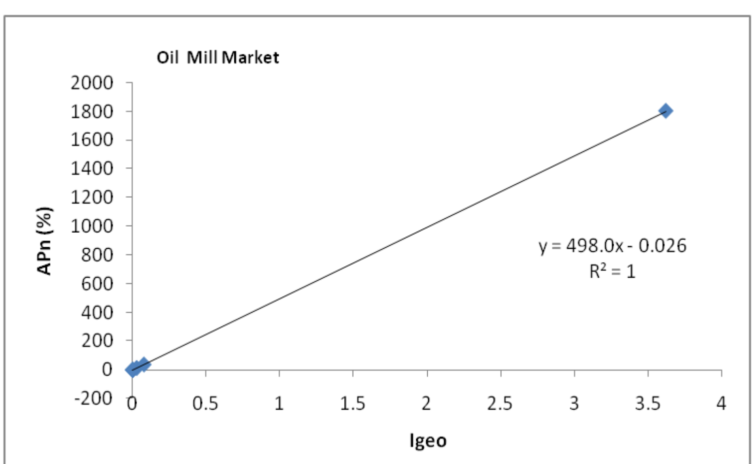
Figure 2(a-d). Bar charts of values for comparing *CF*, I_{geo}, and Apn of the four sampling sites

Generally, the pollution index obtained in this study was less than 1. The contamination level maybe classified based on their intensities on a scale ranging from 1 to 5 (0 = none, 1 = medium, 2 = moderate, 3 = strong, 4 = strongly polluted, 5 = very strongly polluted). The overall pollution status indicates the total pollution of the individual pollution indexes. The result obtained from this study signifies that the top soils from the Port Harcourt are not contaminated with heavy metals. However, the values obtained were significant.

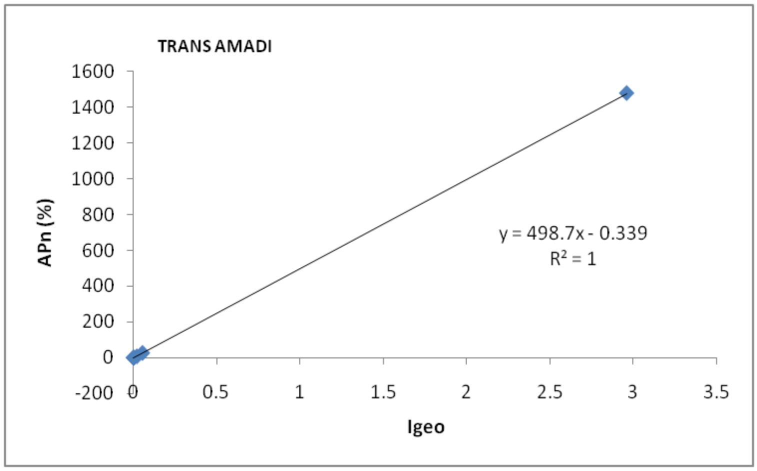
SAR is a widely accepted index for characterizing soil sodicity, which describes the proportion of sodium to calcium and magnesium in a soil solution. SAR values obtained, ranged from 3.02 $(Cmolkg^{-1})^{05}$ at Trans Amadi to 4.25 $(Cmolkg^{-1})^{05}$ at OM Market. The mean of SAR for all Port Harcourt soil was 3.54. This value falls within the typical range of 2.17-8.0 $(Cmolkg^{-1})^{05}$. Higher values of SAR indicate loamy sand, clay loam and clay soil (Alloway, 2002). However, values of adsorption ratios shown in Table 4 indicate that the textural class was neither of the above class. This agrees with the textual class established through particle size distribution. Sodium adsorption ratio is of increasing importance as an index for measuring salinity. Threshold value reported in literature is 12 $(Cmolkg^{-1})^{05}$ (Mohsen *et al*., 2009). In comparison with the threshold, it shows that Port Harcourt soils have low SAR. These suggest that the soils are less sodic. Sodic soils tend to have poor structure with unfavourable physical properties such as poor water infiltration and air exchange, which can reduce plant growth.

3. 4. Chemometric assessment of APn and Geo-accumulation index

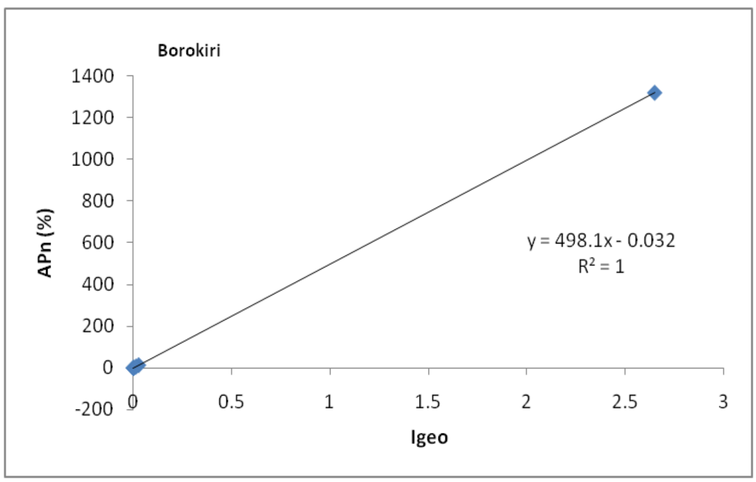
Anthropogenicity (APn), although, similar to Igeo, measures the percentage or extent of anthropogenic input on the environment. The Igeo values obtained in this study were all below zero (0) which indicate uncontamination of the soil, except for, Cd which showed moderate contamination at Borrokiri (2.65) to heavy contamination at Trans Amadi (3.62), as categorized by Edori and Kpee (2017). These suggest that Port Harcourt soils are contaminated by Cd, which is confirmed by the high anthropogenic input (1,320% to 1,803%), as shown in Table 4. Pb, Ni, and Zn were also significant. Ranking in order of decreasing contributions showed Cd>Pb>Ni>Zn>As>Cu>Cr>Fe. Edori and Kpee (2017) observed that certain metals (Cadmium, arsenic, and lead, etc.) are always found in low concentration in the upper layer of the soil, except when there is anthropogenic interference which is in agreement with the findings of this study.



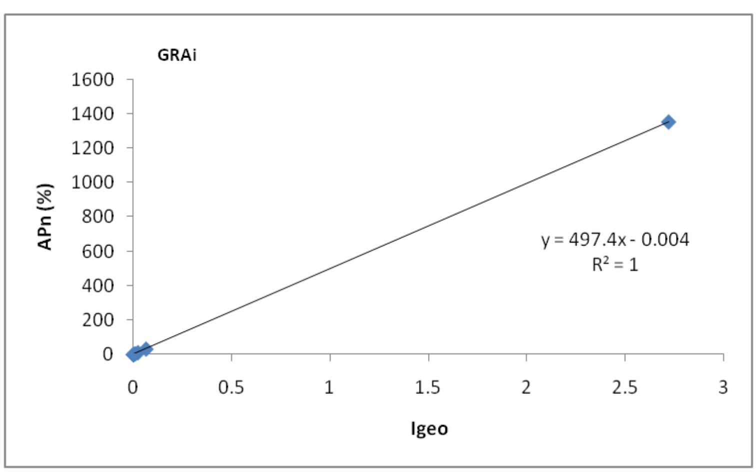
(a)



(b)



(c)



(d)

Figure 3(a-d). Scatter plot showing relationship between I_{geo} and APn in soils of Port Harcourt

The accumulation of these metals in the environment to a large extent is directly caused by anthropogenic activities with (+1) R-value, as shown in **Figure 3** above. Increasing anthropogenic activities will cause increasing geo-accumulation of these metals in the soil. Therefore, there is need to reduce anthropogenic activities, because, these metals are very detrimental to health of plants and animals when in high concentrations, or due to their bio-accumulation tendencies.

4. CONCLUSIONS

The results obtained for the heavy metals in the soils of Port Harcourt indicate that the soil is uncontaminated by these metals, except for Cd and Zn, which showed moderate to heavy contamination. Index models applied to the results of the heavy metals revealed that the source of the metals in the soils were largely from anthropogenic sources. Pearson's correlation analysis revealed that Cd/Na, Cd/Ca, As/K, and Cd/As strongly correlated to each other, which revealed that contamination could be from similar anthropogenic source. Also, the PLI index models confirmed that the soils were unpolluted, they were of no significance. SAR also showed that Port Harcourt soils are less sodic and could be a good soil for plant growth. However, the problem of pollution from these metals in these areas should be under routine check for possible pollution in the near future as some metals showed elevated concentrations above background values.

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